FUNCTIONAL GROUPS CHARACTERISATION OF INDOOR PARTICULATE MATTER IN SCHOOLS

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ABSTRACT

School-age children spend most of the day at school. During this period, and regarding indoor activities, they are exposed to pollutants, namely particulate matter (PM), which can originate from dust re-suspension, furniture, building materials, cleaning activities and be influenced by ventilation rates. Identifying the chemical composition of PM is essential to minimise its effects on human health. Thus, the main aim of this study was to chemically characterise the composition of indoor PM in a pre-school classroom in the PM_{10} fraction. Indoor concentrations of PM_1, $PM_{2.5}$ and PM_{10} were continuously measured in a pre-school classroom for approximately 2.5 days. Indoor hourly mean concentrations were compared with WHO guidelines. Simultaneously, particles were gravimetrically collected for approximately 7 days. FTIR was used to chemically characterise the PM functional groups. The results showed an increase in PM concentration at the beginning of morning activities, which alternates with decreases and increases, according to children's occupation period, as expected. WHO guidelines were exceeded more than 61% of the time for $PM_{2.5}$ and 17% for PM_{10}. FTIR spectra allowed to identify the chemical composition of PM, namely the bands assigned to ammonium, aliphatic carbon, carbonyl group, nitrates, and sulfates. The presence of sulfates (probably ammonium sulfate and more acidic sulfate species) and nitrates (ammonium nitrate), which are formed in the atmosphere, suggests the influence of outdoor air.
Keywords: indoor air quality, particulate matter (PM), FTIR characterization, pre-school classroom, children.

1 INTRODUCTION

Indoor air pollution has been associated with the decline in lung function, being more evident in children, as their organism is still in the development stage [1]. School-age children spend most of the day at school, and during this period, they are exposed to many pollutants, such as particulate matter (PM), carbon monoxide, nitrogen dioxide, ozone, volatile organic compounds and formaldehyde. Many factors can contribute to poor indoor air quality namely, emissions from building materials, furniture, equipment, ventilation system, wear or textile products, consumer products, cleaning and cooking activities [2]–[4].

The study of PM has attracted high interest because of their associated health impacts. Their reduced dimensions allow penetration into the respiratory system. Thus, identifying the chemical composition of PM is essential to minimise its effects on human health.

Typically, PM is composed of nitrates, chlorides, sulfates, metals, ammonium, minerals and carbonaceous material, polycyclic aromatic hydrocarbons (PAH) and metals [5]. Exposure to these substances can cause adverse effects on respiratory health, such as asthma, allergic reactions and lung cancer [6], [7].

Over the last years, many studies have been conducted assessing children exposure to PM in schools, and as expected, most of them showed that indoor PM concentrations depend on children activities, classroom occupancy and outdoor PM concentrations [2], [3], [8], [9]. On the other hand, the few studies that collected particles inside the classrooms and carried out their chemical characterisation attributed their presence to both human (skin flakes) and mineral origin (building materials, chalk and soil material brought by children's shoes) [10].

Although FTIR spectroscopy has been used to characterise the chemical composition of PM both from indoor and outdoor environments [11]–[15], to the best of the authors knowledge, only one study characterised dust settled in different indoor micro-environments of an academic institution in India [16]. Thus, the main aim of this study was to chemically characterise the composition of indoor PM in a Portuguese pre-school classroom in the PM_{10} fraction.

2 MATERIAL AND METHODS

2.1 Sites description

This study was carried out in a pre-school classroom, part of the SENSINAIR project, located in an urban area in Porto district, North of Portugal (41°N, 8°W), next to a road with high traffic density (front) and a residential area (backyard). The main characteristics of the classroom studied are summarised in Table 1.

Table 1: Pre-school classroom description.

Children's age (years)	Floor	Area (m^2)	Average occupancy	Occupant density (occupants /m^2)	Occupancy period	Dust cleaning	Ventilation	Board
5–6	Ground floor	40	18	0.45	9–12 h; 14–18 h	Sweep, vacuum, wash	Natural (keeping the doors and windows open)	Chalkboard

Although the main cleaning activities were performed during and at the end of the occupancy period, alcohol-based disinfectants use, and surfaces cleaning were constant throughout the day because of preventive measures implementation due to COVID-19.

2.2 Sampling and analysis

Indoor PM_1, $PM_{2.5}$ and PM_{10} concentrations were continuously measured using a TSI DustTrak™ DRX 8533 Aerosol Monitor (TSI, USA), with light-scattering, operating at 3 L/min, during a sampling period of approximately 2.5 days. Indoor hourly mean concentrations were compared with WHO guidelines for PM_{10} (50 µg/m^3) and $PM_{2.5}$ (25 µg/m^3) and with Portuguese legislation limits whose values are the same. Simultaneously, particles were gravimetrically collected using internal polytetrafluoroethylene (PTFE) membranes filters with a 2.00 µm pore size and 37 mm diameter, during a sampling period of approximately 7 days. The device was equipped with a size-selective impactor for PM_{10} and was previously calibrated by the manufacturer. Filter weight was measured using an analytical balance (Mettler Toledo AG245 with a reading accuracy of 0.1 mg). Filters were appropriately stored in Petri dishes for consequent chemical analysis.

Infrared (IR) spectra were recorded with a Vertex 70 spectrometer (Bruker), equipped with an ATR cell with a A225/Q PLATINUM ATR Diamond crystal with single reflection accessory. Each spectrum was taken with an average of 64 scans, with a 4 cm^{-1} resolution in the 4000–500 cm^{-1} range.

3 RESULTS AND DISCUSSION

Table 2 summarises the minimum, maximum and mean concentrations of PM_1, $PM_{2.5}$ and PM_{10} measured in the pre-school classroom, and Fig. 1 shows their mean daily profiles.

Table 2: Parameters of the PM hourly mean data.

	Particulate matter hourly mean values ($\mu g/m^3$)		
	PM_1	$PM_{2.5}$	PM_{10}
Minimum	11.00	11.32	12.67
Maximum	57.38	58.27	104.37
Mean	28.45	29.32	36.71

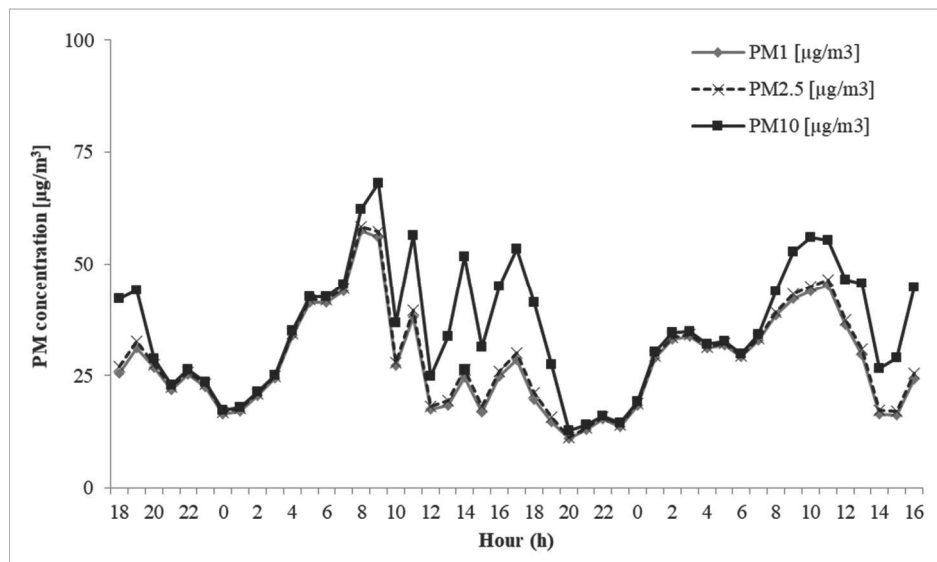
Figure 1: Mean PM_1, $PM_{2.5}$ and PM_{10} daily profile.

As expected, PM concentration profiles were similar among the different fractions, showing an increase in PM concentration at the beginning of morning activities, which alternates with decreases and increases, according to children's occupation period. Furthermore, concentrations decreased during the night after the end of activities and a last increase, possibly related to cleaning activities. Other authors also reported an increase in PM concentration during the beginning of children room occupancy alternated with decreases during the lunch period, when children went to the lunchroom, followed by a new increase until the end of the activities [3], [17].

Usually, the activities performed by the younger children (pre-school) inside the classroom and their greater physical activity combined with a large number of students per room and poor ventilation to maintain thermal comfort contribute to a constant re-suspension of sedimented particles [18]. Furthermore, sweeping during cleaning activities and the presence of a chalkboard clearly increased the PM levels.

To avoid contact between children from different classrooms (due to the SARS-CoV-2 pandemic), the children included in this study had all their meals inside the classroom, hampering the observation of such evident differences in the PM concentrations profiles between the occupancy and non-occupancy periods. This unusual occupation associated with an elevated re-suspension caused by occupants' activities, may have contributed to the fact that both Portuguese legislation limit and WHO guidelines were exceeded around 61% of the time for $PM_{2.5}$ and 17% for PM_{10}.

PM functional groups were chemically characterised by FTIR (Fig. 2). As expected, the typical PTFE bands were observed at 1205, 1149, 639, 554 and 509 cm^{-1} [19]. Excluding these bands, the FTIR spectra allowed to identify the chemical composition of PM, namely the bands at 3286 (NH_4^+, antisymmetric stretching) and 1410 cm^{-1} corresponding to ammonium and two bands at 2918 and 2850 cm^{-1} assigned to aliphatic carbon (CH stretching). The presence of amides can be attributed to the rubber of sneakers (shoe sole), as it is one of its main constituents [16], [20], while the presence of CH compounds, namely, alkanes and phthalate esters, may be attributed to cooking activities and floor polishes [14]. Furthermore, Sahu et al. [16] reported that the particles found in dust were soot, minerals, gypsum and the functional groups identified by FTIR (mainly alkyl halide and alkane), confirmed the presence of VOC (volatile organic carbon) in indoor dust.
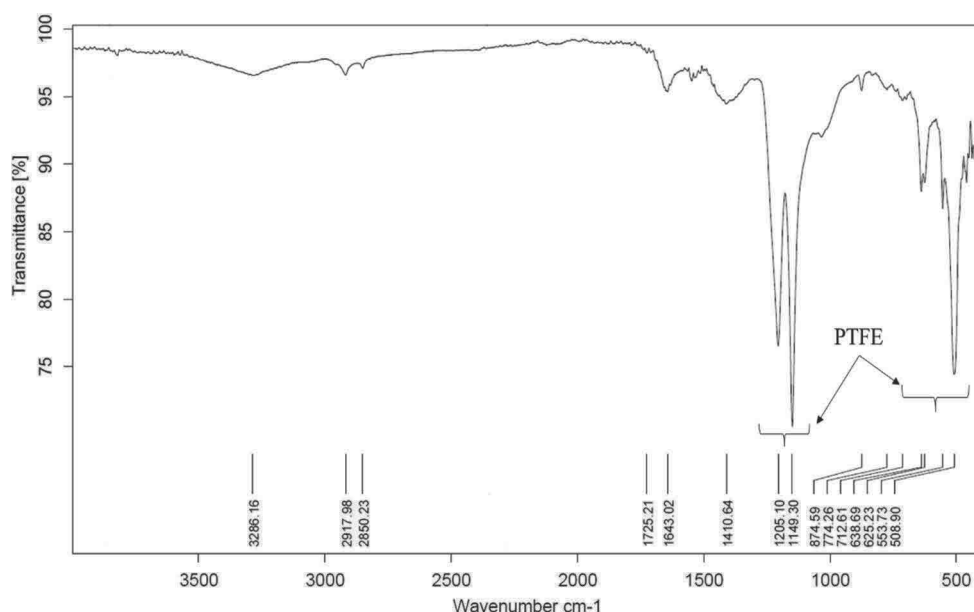

Figure 2: FTIR spectrum of the collected particles.

The carbonyl group band (C=O stretching) at 1725 cm^{-1}, typical of aliphatic aldehydes, ketones and carboxylic acids, was also observed. Finally, the organic nitrate at 1643 cm^{-1} (N-H, bending), the inorganic nitrate at 874 cm^{-1} and the shoulder at 1100 cm^{-1} assigned to sulphates (S=0, stretching) were also identified. The presence of sulfates (probably ammonium sulfate and more acidic sulfate species), and nitrates (ammonium nitrate), which are formed in the atmosphere from the photochemical oxidation of NO_x and SO_2, suggests

the influence of outdoor air [12], [14]. These findings are in accordance with Reff et al. [14] and Estokova et al. [11].

4 CONCLUSIONS

This study allowed to chemically characterise the composition of indoor PM in a Portuguese urban pre-school classroom in the PM_{10} fraction, using FTIR spectra.

The main bands identified were assigned to ammonium, aliphatic carbon, carbonyl group, sulphates, organic and inorganic nitrate. The presence in indoor samples of sulfates (probably ammonium sulfate and more acidic sulfate species), and nitrates (ammonium nitrate), which are formed in the atmosphere, suggests that outdoor sources influenced the indoor air.

Globally, PM concentration profiles were similar among the different fractions and WHO guidelines were exceeded around 61% of the time for $PM_{2.5}$, and 17% for PM_{10}. These exceedances may be attributed to the presence of many students associated with a poor ventilation system. In addition, the use of a chalkboard, their classroom walking activities and having meals inside the classroom may have contributed to increasing PM accumulation, leading to an elevated re-suspension.

REFERENCES

[1]   Sram, R.J. et al., Health impact of air pollution to children. *Int. J. Hyg. Environ. Health*, **216**(5), pp. 533–540, 2013.

[2]   Guo, H., Morawska, L., He, C., Zhang, Y.L., Ayoko, G. & Cao, M., Characterization of particle number concentrations and $PM_{2.5}$ in a school: Influence of outdoor air pollution on indoor air. *Environ. Sci. Pollut. Res.*, **17**(6), pp. 1268–1278, 2010.

[3]   Nunes, R.A.O., Branco, P.T.B.S., Martins, F.G. & Sousa, S.I.V., Particulate matter in rural and urban nursery schools in Portugal. *Environ. Pollut.*, **202**, pp. 7–16, 2015.

[4]   Perrino, C., Tofful, L. & Canepari, S., Chemical characterization of indoor and outdoor fine particulate matter in an occupied apartment in Rome, Italy. *Indoor Air*, **26**(4), pp. 558–570, 2016.

[5]   Kelly, F.J. & Fussell, J.C., Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. *Atmos. Environ.*, **60**, pp. 504–526, 2012.

[6]   Zhang, L. et al., Personal exposure measurements of school-children to fine particulate matter ($PM_{2.5}$) in winter of 2013, Shanghai, China. *PLoS One*, **13**(4), pp. 1–16, 2018.

[7]   Xu, D. et al., Acute effects of ambient $PM_{2.5}$ on lung function among schoolchildren. *Sci. Rep.*, **10**(1), pp. 1–8, 2020.

[8]   Vilcekova, S., Meciarova, L., Burdova, E.K., Katunska, J., Kosicanova, D. & Doroudiani, S., Indoor environmental quality of classrooms and occupants' comfort in a special education school in Slovak Republic. *Build. Environ.*, **120**, pp. 29–40, 2017.

[9]   Branco, P.T.B.S., Alvim-Ferraz, M.C.M., Martins, F.G., Ferraz, C., Vaz, L.G. & Sousa, S.I.V., Impact of indoor air pollution in nursery and primary schools on childhood asthma. *Sci. Total Environ.*, **745**, 2020.

[10]   Rovelli, S. et al., Airborne particulate matter in school classrooms of northern Italy. *Int. J. Environ. Res. Public Health*, **11**(2), pp. 1398–1421, 2014.

[11]   Estokova, A. & Stevulova, N., Investigation of suspended and settled particulate matter in indoor air chapter. *Intech*, pp. 455–480, 2012.

[12]   Sreejith, M.V., Thomas, J.R., Aravindakumar, C.T. & Aravind, U.K., Characterisation of atmospheric particulate matter over a site in southern Kerala, India: Using ATR-FTIR and confocal micro-raman spectroscopy. *Mater. Today Proc.*, **33**, pp. 1410–1414, 2019.

[13]   Reff, A. et al., Functional group characterization of indoor, outdoor, and personal $PM_{2.5}$: Results from RIOPA. *Indoor Air*, **15**(1), pp. 53–61, 2005.

[14]   Reff, A. et al., A functional group characterization of organic $PM_{2.5}$ exposure: Results from the RIOPA study. *Atmos. Environ.*, **41**(22), pp. 4585–4598, 2007.

[15]   Radulescu, C., Stihi, C., Iordache, S., Dunea, D. & Dulama, I.D., Characterization of urban atmospheric $PM_{2.5}$ by ATR-FTIR, ICP-MS and SEM-EDS techniques. *Rev. Chim.*, **68**(4), pp. 805–810, 2017.

[16]   Sahu, V., Elumalai, S.P., Gautam, S., Singh, N.K. & Singh, P., Characterization of indoor settled dust and investigation of indoor air quality in different micro-environments. *Int. J. Environ. Health Res.*, **28**(4), pp. 419–431, 2018.

[17]   Juliana, P.S., Branco, P.T.B.S., Alvim-Ferraz, M.C.M., Martins, F.G. & Sousa, S.I.V., Evaluation of low-cost mitigation measures implemented to improve air quality in nursery and primary schools. *Environ. Res. Public Heal.*, pp. 14–17, 2017.

[18]   Branco, P., Alvim-Ferraz, M., Martins, F. & Sousa, S., Indoor air quality in urban nurseries at Porto city: Particulate matter assessment. *Atmos. Environ.*, **84**, pp. 133–143, 2014.

[19]   Fazullin, D.D., Mavrin, G.V., Sokolov, M.P. & Shaikhiev, I.G., Infrared spectroscopic studies of the PTFE and nylon membranes modified polyaniline. *Mod. Appl. Sci.*, **9**(1), pp. 242–249, 2015.

[20]   Martín-Martínez, J.M., Shoe industry. *Handbook of Adhesion Technology*, eds L.F.M. da Silva, A. Öchsner & R.D. Adams, Springer, Berlin, Heidelberg, 2011.